isotropic g behavior as would be expected if there is some distortion away from the square-pyramidal symmetry and/or relaxation of the dominance of the ligand field by the V–O multiple bond. While this anisotropy is not resolvable, the oriented liquid crystal spectra show much more clearly the anisotropic character of the perpendicular bands (Figure 9). There is enhancement of individual bands upon rotating the sample tube as seen for $VO(acac)_2$. The calculation of g_x and g_y shows them to be very close, whereas A_x and A_y are quite different (Table II). By analogy with the $VO(acac)_2$ spectrum the assignment given was made.

Optically Active Complexes. Buckingham and coworkers[39] and Stegemeyer and Mainusch[40] have shown that nematic liquid crystals containing optically active solutes can become cholesteric in their behavior (*i.e.*, rotate circularly polarized light). As the amount of optically active solute is increased the properties of the liquid crystals gradually shift from nematic to cholesteric, removing the possibility for their use in optical measurements. A further result was that even at the highest field used (5.9 kG) there was incomplete ordering even after a period of 10 min.[40] In the presence of mesotartaric acid, however, the orientation was complete. Solutions of racemic tartaric acid or racemic menthol produced no cholesteric properties.

The epr studies presented here show clearly that reasonable magnetic parameters are obtained even from optically active solutes. The epr spectra of $VO(sal)_2(+)pn$ and its racemic mixture are identical with no difference in their orientation properties. While there appears to be incomplete ordering with $VO(sal)_2(+)tnCH_3$ the magnetic tensors are readily obtained.

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Partially Relaxed Fourier Transform Boron-11 Nuclear Magnetic Resonance Spectra. Resolution Enhancement in the Spectrum of *n*-Nonaborane(15)[1]

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Abstract: Partially relaxed Fourier transform (PRFT) ^{11}B nmr spectra, obtained by means of the 180–90° rf pulse sequence, are used for studying boron compounds in solution. Variations in ^{11}B spin–lattice relaxation times within a molecule cause intensity differences in a PRFT spectrum. In favorable cases, these intensity differences can be used to extract heretofore unresolved lines. For example, the downfield triplet of decaborane(14) is resolved into its two component doublets. The previously hidden $B(3)H_2$ triplet in *n*-nonaborane(15) is resolved by the PRFT method. PRFT spectra also provide evidence for deuteration at B(3) of $n\text{-}B_9H_{15}$ in the exchange reaction of this compound with B_2D_6.

Fourier transform (FT) nmr[2] is being used increasingly[3] as a preferable alternative to continuous-wave nmr, not only because of the increased sensitivity of the FT method[2] but also because of the additional information that is often available from partially relaxed Fourier transform[4] (PRFT) spectra.[5,6] The PRFT technique is an extension of the old 180°–90° rf pulse method of Hahn[7a] and Carr and Purcell[7b] for measuring spin–lattice relaxation times (T_1). Until recently, measurements by means of the 180°–90° pulse sequence yielded only average T_1 values for various nonequivalent nuclei of the same spin species. In 1968, Vold and coworkers[4] showed that the 180°–90° pulse sequence could be used to measure individual T_1 values of resolved resonances by applying a Fourier transformation to the signal following the 90° pulse. Recently, Allerhand and coworkers have used carbon-13 PRFT spectra for studying the details of molecular motion of large organic molecules[5a,b] and biopolymers.[5c] We show below that ^{11}B PRFT spectra provide, in favorable cases, structural information that may not be available from normal spectra.

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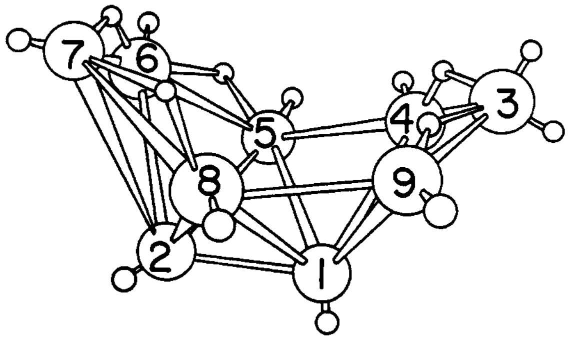

Figure 1. Structure of *n*-nonaborane(15).

In the PRFT technique,[4] the equilibrium longitudinal magnetization in the absence of a radiofrequency field (M_0) is first inverted into $-M_0$ by means of a 180° rf pulse. For an interval τ the magnetization is allowed to decay to some value intermediate between $-M_0$ and M_0. Then a 90° rf pulse is applied for the purpose of tilting the magnetization into the plane perpendicular to the static magnetic field, where it can be measured by conventional nmr phase-sensitive detection devices. The resulting time-domain signal is Fourier transformed to yield a partially relaxed frequency domain spectrum. If the decay of the longitudinal magnetization of a particular resonance is exponential, then the amplitude A of that resonance in a PRFT spectrum is given by[7]

$$A = A_0[1 - 2\exp(-\tau/T_1)] \qquad (1)$$

where A_0 is the equilibrium amplitude measured in a normal FT spectrum (resulting from a sequence of 90° rf pulses separated by intervals long compared with T_1) and T_1 is the spin–lattice relaxation time for the particular resonance. It follows from eq 1 that a resonance will appear inverted, nulled, or positive (with respect to the normal spectrum) depending on whether τ is smaller, equal to, or larger than $T_1 \ln 2$, respectively. Thus, if two resonances have different T_1 values, their spectral amplitudes will have a different dependence on τ.

We wish to point out that, as in ^{13}C nmr, PRFT ^{11}B spectra can be useful in studies of chemical structure only if there is appreciable variation of T_1 values between the various ^{11}B nuclei. It is thus pertinent to consider ^{11}B spin–lattice relaxation mechanisms. Theoretical considerations[8] and experimental results[9] indicate that we need only consider quadrupolar relaxation. In this case, T_1 for a spin-$^3/_2$ nucleus is given by[8]

$$1/T_1 = \frac{1}{10}(eQq)^2\left(1 + \frac{1}{3}\eta^2\right)\tau_{\text{eff}} \qquad (2)$$

where eQq is the quadrupole coupling constant,[10] η is the asymmetry parameter,[10] and τ_{eff} is an effective rotational correlation time. Both eQq and η depend on the electric field gradient tensor at the nucleus[10] (a molecular electronic property) and are practically independent of solvent and temperature.[10] On the other hand, τ_{eff} depends on the size and shape of the molecule and on solvent–solute and solute–solute interactions. Consequently, τ_{eff} and T_1 are *solvent* and *temperature* dependent. Differences in τ_{eff} for *different nuclei in one molecule* may arise from anisotropy in the rotational reorientation[11] (when the molecular shape is far from spherical) or from the presence of internal motion.[12] We expect no major differences in τ_{eff} for the various ^{11}B nuclei in the same polyhedral borane. The observed[9,13] variations in ^{11}B T_1 values within the same molecule must arise mainly from differences in the electric field gradient tensor at the boron nuclei.

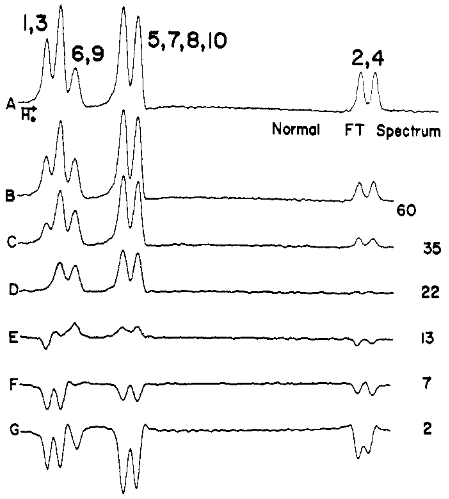

Figure 2. Boron-11 nmr spectra of 1 *M* decaborane(14) in CS_2 obtained by the Fourier transform method, with 2048 points in the time domain and 5000-Hz sweep width. Each spectrum is the result of 128 accumulations with a recycle time of about 0.3 sec (total time about 0.7 min): (A) Normal spectrum. Assignments of the resonances are given above the peaks. Chemical shifts and coupling constants (δ, ppm, relative to $BF_3 \cdot O(C_2H_5)_2$ (J, Hz)) are: B(1,3), −11.8 (150); B(6,9), −9.7 (155); B(5,7,8,10), −0.3 (160); and B(2,4), +36.1 (155). (B–G) Representative PRFT spectra, with τ values indicated in msec.

Conventional ^{11}B nmr spectroscopy has been a powerful aid for elucidating solution structures, identifying substitution sites, and studying interconversion processes of polyhedral boranes.[14] However, ^{11}B nmr spectra of polyhedral boranes usually consist of resonances with linewidths of 60–100 Hz at room temperature.[14] As a consequence, nearly always the only observable splittings from ^{1}H–^{11}B scalar coupling are those from directly bonded terminal hydrogens. In addition, terminal ^{1}H–^{11}B coupling constants of polyhedral boranes are relatively invariant, in the range 120–180 Hz.[14] This combination of factors often leads to accidental overlap of ^{11}B resonances from nonequivalent borons, which creates ambiguities in spectral interpretation. The use of high magnetic fields (51.7 kG, 70.6 MHz), and proton decoupling by means of noise-modulated ^{1}H excitation can in some cases considerably improve the resolution in ^{11}B spectra.[15] We show below a case in which a high magnetic field and

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proton decoupling still yield ambiguous spectra, but that the ambiguity can be removed by means of PRFT spectra. Specifically, we deal with a heretofore unresolved problem in the spectrum of *n*-nonaborane(15).

Although the crystal structure of *n*-B_9H_{15} (Figure 1)[16] has been known for some time, low-field ^{11}B nmr spectra of *n*-B_9H_{15} *in solution* failed to reveal the 1:2:1 triplet (relative intensity 1) arising from the lone $B(3)H_2$ group.[17,18] Even a recent high-field (64.2 MHz) ^{11}B nmr spectrum[19] and a proton-decoupled 70.6-MHz spectrum[18] display only 1:2:3:2:1 patterns of doublets. The 220-MHz pmr spectrum of *n*-B_9H_{15} clearly indicates two bridge proton resonances (relative intensities 2 and 3),[18] which is compatible with a static solution structure. Rationalizations of the ^{11}B nmr spectra involving tautomerism of all bridging hydrogens, as in B_6H_{10},[20] or only a fraction of the bridging protons, as suggested for B_8H_{12},[21] are difficult to postulate in light of this pmr spectrum.

This paper introduces the technique of PRFT ^{11}B nmr spectroscopy and demonstrates the ability of the PRFT technique to show the presence of the heretofore unobservable BH_2 triplet of *n*-B_9H_{15}, hidden under the main body of the ^{11}B spectrum through accidental overlap of all three peaks with other resonances.

Experimental Section

The equipment consisted of a "home-built" pulsed nmr apparatus operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, a Fabri-Tek 1074 signal averager, and a PDP-8/I computer. Additional details have been given elsewhere.[5a]

Standard high-vacuum techniques were used for sample preparation. *n*-Nonaborane(15) of normal isotopic abundance (80.42% ^{11}B, 19.58% ^{10}B) was prepared by the hot-cold flow quench reaction of B_2H_6 and B_5H_9[22] and purified by fractional crystallization and low-temperature, high-vacuum distillation. Purity was monitored by means of ^{11}B nmr spectra. Isotopically labeled *n*-nonaborane(15), *n*-$^{10}B^{n}B_8H_{15}$, was prepared by the reaction of 3 mmol of $^{n}B_8H_{12}$ and 5.75 mmol of $^{10}B_2H_6$ (96% ^{10}B enriched, Oak Ridge National Laboratories, Oak Ridge, Tenn.) in a 5-ml Pyrex bomb held at −30° for 6 hr.[23] Repeated low-temperature columning produced a material whose ^{11}B nmr resonances were in the ratios 0.93:3.98:2.01:1.08 (theoretical ratios for *n*-$^{n}B_9H_{15}$ are 1:5:2:1), indicating one specific ^{10}B label per molecule (in the large downfield multiplet) with little or no scrambling. PRFT ^{11}B nmr spectra of *n*-$^{10}B^{n}B_8H_{15}$ and *n*-$^{n}B_9H_{15}$ were run on 25% v/v solutions in *n*-pentane. The partially deuterated *n*-nonaborane, *n*-$B_9H_{10.1}D_{4.9}$, is the actual sample from ref 23, and resulted from the exchange reaction of *n*-B_9H_{15} with excess liquid B_2D_6 at 27° for 24 hr. PRFT ^{11}B nmr spectra were run on a 30% v/v solution in CS_2. Decaborane was sublimed before use.

Results and Discussion

It is instructive to consider first the application of the PRFT method to a problem with a known solution: the origin of the downfield triplet in the 70.6-MHz ^{11}B spectrum of decaborane. It is known[14b,24] that this triplet arises from the accidental overlap of two BH doublets and not, of course, from a BH_2 group. A set of ^{11}B PRFT spectra of 1 *M* decaborane in CS_2 is shown in Figure 2. The upfield doublet (of the ordinary spectrum) behaves "normally" in the PRFT spectra; that is, it remains a 1:1 doublet, with both peaks negative at τ <20 msec, nulled at $\tau \approx 20$ msec, and positive at τ >20 msec. The behavior of the downfield doublet is also "normal," with a null at $\tau \approx 10$ msec. The downfield triplet, however, does not remain a triplet in some of the PRFT spectra (Figure 2). The nonequivalent borons giving rise to the two overlapping doublets in this triplet happen to have *appreciably different* T_1 *values*, so that the two doublets are nulled at different τ values (about 7 and 22 msec, respectively). Thus, when one records the PRFT spectrum with $\tau/\ln 2$ chosen equal to T_1 of the 1,3 borons (about 22 msec), the resonances of these borons are nulled and the spectrum clearly shows the resonances of the 6,9 borons. If the downfield signal were a true BH_2 triplet, it would remain a triplet in all the PRFT spectra.

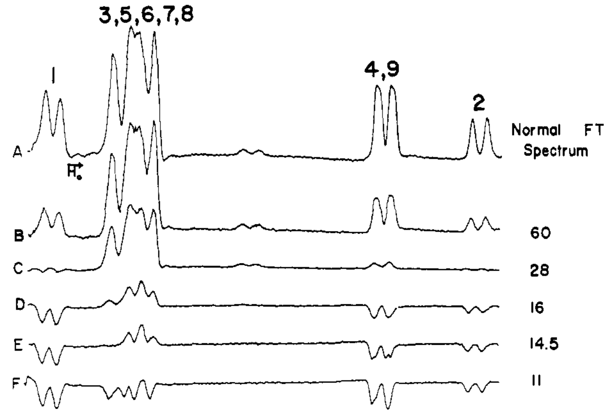

Figure 3. Boron-11 nmr spectra of *n*-nonaborane(15) in *n*-pentane obtained by the Fourier transform method, with 2048 points in the time domain and 5000-Hz sweep width. (A) Normal spectrum resulting from 1024 accumulations with a recycle time of 0.25 sec. Assignments of the resonances are given above the peaks. Chemical shifts and coupling constants (δ, ppm, relative to $BF_3 \cdot O(C_2H_5)_2$ (*J*, Hz)) are: B(1), −17.2 (155); B(5,8 or 6,7), −7.1 (170); B(6,7 or 5,8), −3.3 (150); B(3), −3.5 (125); B(4,9), +32.9 (155); and B(2), +47.5 (165). (B–F) Representative PRFT spectra, each resulting from 2048 accumulations with recycle times of about 0.3 sec. τ values are indicated in msec.

A set of ^{11}B PRFT spectra of *n*-B_9H_{15} is shown in Figure 3. At τ 14.5 msec, the strong downfield multiplet is nearly nulled, showing only an apparent triplet with relative intensities not quite 1:2:1, and with adjacent line separations of 125 Hz (Figure 3E). A tentative interpretation (confirmed below) is that the triplet arises from a BH_2 group which happens to have a ^{11}B T_1 value appreciably shorter than all the other borons in the multiplet. Thus, the PRFT method unravels a spectral feature not visible in the normal nmr spectrum. At this point we caution against overenthusiastic use of the PRFT technique. It is conceivable that the triplet in Figure 3E is the result of two overlapping doublets, although this would imply an unusually small ^{11}B–^{1}H coupling constant for a BH group. The observed splitting of 125 Hz is consistent with known ^{11}B–^{1}H coupling constants of BH_2 groups.[14] It should be noted that the triplet in Figures 3D and 3E does not have exactly 1:2:1 relative intensities because not all the other borons in the multiplet are perfectly nulled with the same τ value.

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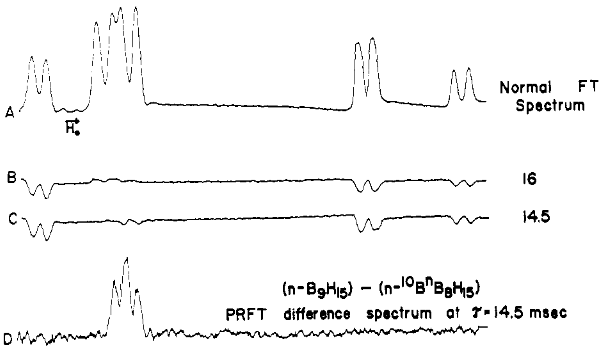

Figure 4. Boron-11 nmr spectra of n-$^{10}B^nB_8H_{15}$ in n-pentane obtained by the Fourier transform method, with 2048 points in the time domain and 5000 Hz sweep width. (A) Normal spectrum resulting from 1024 accumulations with a recycle time of 0.25 sec. (B and C) PRFT spectra resulting from 2048 accumulations with τ 16 and 14.5 msec, respectively. (D) "Difference" spectrum of Figure 3E minus Figure 4C showing triplet arising from B(3) group (δ −3.5 ppm, relative to $BF_3 \cdot O(C_2H_5)_2$, J = 125 Hz).

In view of the novelty of the PRFT method in studies of polyhedral boranes, we decided to obtain further evidence for our interpretation of the ^{11}B PRFT spectra of n-B_9H_{15}. In Figure 4 we show the normal FT ^{11}B nmr spectrum and two PRFT spectra of n-nonaborane(15) 96% enriched with ^{10}B at position 3. The spectra were obtained on a sample in the same solvent and with the same concentration as was used for n-B_9H_{15} of normal isotopic abundance, so that there would be no changes in T_1 from a difference in viscosity between the two samples. The PRFT spectra in Figures 4B and 4C do not show the triplet observed in the corresponding PRFT spectra of n-B_9H_{15} of normal isotopic abundance (Figures 3D and 3E, respectively). This confirms our interpretation.

Figure 4D is the result of digitally subtracting the spectrum in Figure 4C from that in Figure 3E. This "difference" spectrum shows the pure $B(3)H_2$ triplet with no residual signal from the BH doublets.

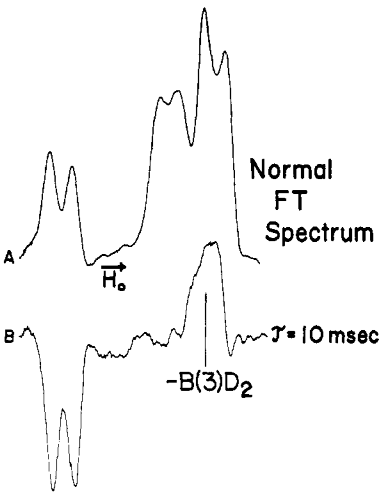

Figure 5. Boron-11 nmr spectra of n-$B_9H_{10.1}D_{4.9}$ in CS_2 obtained by the Fourier transform method, with 2048 points in the time domain, recycle times of 0.25 sec, and 5000-Hz sweep width. (A) Low-field resonances of nomal spectrum resulting from 1024 accumulations. (B) PRFT spectrum resulting from 2048 accumulations, with τ 10 msec, showing exhaustive deuteration at B(3).

We have also applied the PRFT method to the partially deuterated n-nonaborane(15) formed from the exchange reaction of n-B_9H_{15} and B_2D_6.[23] In Figure 5A we show the downfield multiplet in the normal spectrum of this compound, and in Figure 5B we show a PRFT spectrum with τ chosen to minimize the signals of B(5,6,7,8). The latter spectrum directly indicates the presence of a $B(3)D_2$ group, which had only been inferred in previous studies.[23]

Additional applications of the PRFT technique to boron chemistry will be reported elsewhere.

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